



NANOSTRUCTURES INCLUDING A METAL

BACKGROUND OF THE INVENTION

The present invention relates to nanostructures and nanostructure formation techniques, and more particularly, but not exclusively, relates to metallic nanowires.

With the constantly decreasing feature sizes of integrated circuits and other microscale devices, the need for increasingly fine patterning of such features present several challenges. Among these challenges is the need to provide various nanostructures, including electrically conductive nanowires. One of the schemes to fabricate nanowires utilizes a lithographic pattern to define an array of closely spaced nanowires that are deposited by chemical vapor deposition or another technique. One drawback of this approach is that lithographic patterning is limited in terms of size and tolerance in the nanometer range.

A related scheme involves filling arrays of channels or pores in a substrate with a material of interest by chemical or electrochemical processes. With this method, it is difficult to continuously fill pores having a relatively long length and small diameter with a desired material having high density. In some instances, to adequately fill the pores, high pressure and high temperature injection of molten metals has been used; however, the fabrication of nanowires from small pores with long length frequently becomes undesirable because of the extreme pressure/temperature involved. Attempts to lower the processing pressure by modifying the composition or surface property of the substrate pores have the further limitation of being applicable with only low melting point metals.

Another scheme bombards a material with ions to form tracks into which the nanowire material is deposited. The track-bearing material is then at least partially removed, leaving the exposed nanowires. U.S. Patent No. 6,444,256 B1 to Musket et al. provides further background information regarding this approach. Such schemes are complicated by the need to remove the material that defined the tracks. A similar drawback arises for other approaches that utilize a template to define channels or pores for forming nanostructures.

A step-edge decoration method has been reported to grow freestanding nanowires, where Mo oxide wires were electrodeposited at step edges on a graphite surface and reduced in H₂ to produce metal. This method is not applicable to produce noble metals, including gold (Au), silver (Ag), platinum (Pt), and copper (Cu), which typically do not nucleate along step edges on graphite to form nanowires. Another method reported is to synthesize Au, Ag and Pt nanowires using reducing and sacrificing templates. Neither step-edge decoration nor sacrificing template methods are capable of producing vertically aligned freestanding metal nanowires. Still other schemes involve a catalyst to provide for the freestanding deposition of carbon nanotubes to which a metallic coating may then be applied. U.S. Patent 6,340,822 B1 to Brown et al. provides further background regarding this approach. These schemes all fail to provide for the growth of freestanding nanowires comprised of metals without complicated post-growth processing. Thus, there is a demand for further contributions in this area of technology.

SUMMARY

As used herein "freestanding" refers to the capability of vertically extending from a base or substrate without support from a template or patterning device. As used herein, "monocrystalline" refers to a solid material having more than 90% by weight organized
5 in a single crystal structure that may include low angle twisting.

One embodiment of the present invention includes a unique technique of providing nanostructures. Other embodiments include unique methods, systems, devices, and apparatus involving nanostructures.

A further embodiment includes depositing a number of nanostructures on a
10 substrate from a organometallic vapor. The nanostructures are composed of material including a metal, at least some of which is deposited from the vapor. In one form, the nanostructures define nanowires that are freestanding during deposition. Additionally or alternatively, the nanostructures are each monocrystalline.

Still a further embodiment of the present invention includes forming a number of
15 nanostructures on a substrate with a organometallic vapor including copper. The nanostructures are freestanding during formation. For one form, the nanostructures each have a first dimension of 500 nanometers or less and a second dimension extending from the substrate to a respective free end of each of the nanostructures which is at least 10 times greater than the first dimension.

20 Yet another embodiment of the present invention includes growing a number of monocrystalline nanowires on a substrate from an organometallic vapor including copper and providing the nanowires with a first dimension of 500 nanometers or less after growth.

Another embodiment of the present invention includes a substrate and a plurality of freestanding nanostructures attached to the substrate that are each monocrystalline and comprised of copper. In one form, the nanostructures each extend from a dielectric surface of the substrate. In other forms, the nanostructures extend from a metallic or semiconductor surface of the substrate. Alternatively or additionally, the nanostructures are in the form of nanowires that each include a respective free end and have a first dimension of 500 nanometers or less and a second dimension extending from the substrate to the respective free end that is at least 10 times greater than the first dimension.

One object of the present invention is to provide a unique technique for providing nanostructures.

Another object of the present invention includes a unique method, system, device, or apparatus involving a nanostructure.

Further objects, forms, embodiments, benefits, advantages, features, and aspects of the present invention shall become apparent from the description and drawings contained herein.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 is a diagrammatic view of a nanostructure formation system.

FIG. 2 is a flow chart of a process that can be performed with the system of FIG.

5 1.

FIG. 3 is a partial, diagrammatic view of a work piece including nanostructures provided in accordance with the process illustrated by the flow chart of FIG. 2.

FIG. 4 is a diagrammatic view of a integrated circuit device including one or more nanostructures.

10 FIG. 5 is a diagrammatic view of a display device including one or more nanostructures.

FIG. 6 is a diagrammatic view of a device for processing signals with a frequency of 100 GigaHertz (GHz) or more including one or more nanostructures.

15 FIG. 7 is a diagrammatic view of a sensing device including one or more nanostructures.

FIG. 8 is a Scanning Electron Microscope (SEM) image of copper nanowires grown on brass in accordance with a First Experimental Example of the present invention.

20 FIG. 9 is a graph depicting an X-ray Photoelectron Spectroscopy (XPS) analysis of copper nanowires formed in accordance with the present invention.

FIG. 10 is a Transmission Electron Microscopy (TEM) image of a copper nanowire formed in accordance with the present invention.

DETAILED DESCRIPTION

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will, nevertheless, be understood that no
5 limitation of the scope of the invention is thereby intended. Any alterations and further modifications in the described embodiments and any further applications of the principles of the invention as described herein are contemplated as would normally occur to one skilled in the art to which the invention relates.

One embodiment of the present invention is a technique to provide metal-
10 containing nanostructures. In one example, a freestanding nanostructure is grown on a substrate by Chemical Vapor Deposition (CVD) using an organometallic substance without a catalyst or reducing agent. The nanostructure is composed of an elemental metal, an alloy of two or more different types of metal, and/or includes one or more types of metal in combination with intermetallics and/or nonmetals, such as oxygen. The
15 substrate can be comprised of a metallic material, intermetallic material, semiconductor, dielectric material, a combination of these, and/or a different material as would occur to those skilled in the art. In a further embodiment, freestanding nanowires are formed on a substrate through a deposition process with the substrate temperature being 400°C or less. This deposition process can include forming the nanowires with an organometallic
20 substance including copper.

Other examples and embodiments of the present invention are described in connection with nanostructure formation system 20 depicted in FIG. 1. System 20 includes processing chamber 22 coupled to pressure control subsystem 24 and

temperature control subsystem 26. Pressure control subsystem 24 regulates gas pressure in chamber 22. Temperature control subsystem 26 includes heating device 54 within chamber 22 to regulate temperature of a work piece and/or other chamber contents.

Chamber 22, subsystem 24, and subsystem 26 are arranged in a standard manner to

5 facilitate Chemical Vapor Deposition (CVD), and/or plasma-assisted CVD procedures.

System 20 also includes deposition material source 30 and oxygen source 40. Deposition material source 30 includes evaporation device 32 to generate a deposition vapor. Source

30 is coupled to chamber 22 by valve 34 that is adjustable in a standard manner to

selectively provide vapor from source 30 to chamber 22. Oxygen source 40 is coupled to

10 chamber 22 by valve 44. Valve 44 is adjustable to selectively provide oxygen (O₂) to

chamber 22. In other embodiments, source 40/valve 44 may be used for the selective introduction of one or more other types of gaseous materials as an addition or alternative

to oxygen. Also, other gaseous materials such as a carrier gas, like Argon (Ar), or other processing materials can be provided in system 20 (not shown). For example, system 20

15 can include a plasma generation/source, a Physical Vapor Deposition (PVD) subsystem, an ion implantation arrangement, and/or different processing equipment as would occur to those skilled in the art.

System 20 includes work piece 50 engaged to work piece holding device 51.

Work piece 50 includes substrate 52. A portion of work piece 50 is shown in greater

20 detail in FIG. 3, which is described hereinafter in connection with process 120 of FIG. 2.

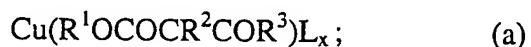
Referring to FIGS. 2 and 3, process 120 can be performed with system 20. Process 120

begins in stage 122 with the preparation of system 20 and substrate 52 to perform

material deposition. Stage 122 also includes placing substrate 52 in chamber 22. Process

120 proceeds from stage 122 to stage 124. In stage 124, pressure control subsystem 24 and temperature control subsystem 26 are utilized to provide appropriate gas pressure and temperature with system 20. In one form, pressure is maintained in a range between about 0.1 torr and about 1.0 torr with pressure control subsystem 24. Temperature control subsystem 26 is utilized to regulate temperature of substrate 52. In one preferred embodiment of this aspect of the invention, nanostructures are formed on a substrate from an organometallic vapor at a substrate temperature of less than 400°C. In a more preferred embodiment, this temperature is in a range between about 200°C and about 400°C. In other embodiments, the pressure, temperature, and/or different parameters are regulated and varied as would occur to those skilled in the art to achieve a desired result. From stage 124, process 120 continues in stage 126 with evaporation of a source material to provide a desired organometallic deposition vapor. This vapor is utilized to deposit a metal constituent on substrate 52.

In one preferred embodiment of the present invention directed to the formation of nanostructures that include copper (Cu), the vapor is provided in the form of an organometallic having copper as a metal constituent. In one more preferred embodiment directed to nanostructure formation with copper, an organometallic compound is utilized corresponding to formula (a) as follows:



where:

R^1 is a C_1 - C_9 hydrocarbyl group;

R^2 is hydrogen (H), fluorine (F), or a C_1 - C_9 hydrocarbyl group;

R^3 is a C_1 - C_9 hydrocarbyl group or an alkylsilane group of the formula $\{-Si(R^4)(R^5)(R^6)\}$, in which R^4 , R^5 , and R^6 are each H, F, a C_1 - C_9 hydrocarbyl group, or a C_1 - C_9 alkoxy group of the formula $\{-OR\}$, in which R is a C_1 - C_9 hydrocarbyl group bonded to silicon (Si);

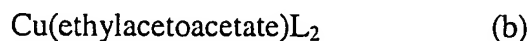
5 x is 1, 2, or 3; and

L is a ligand including phosphorus (P) of the formula $\{P(R^7)(R^8)(R^9)\}$, in which R^7 , R^8 , and R^9 are each a hydroxy group, a C_1 - C_9 hydrocarbyl group, or an alkoxy group of the formula $\{-OR\}$, in which R is a C_1 - C_9 hydrocarbyl group.

10 As used herein, " C_1 - C_9 " means that the number of carbons (C) in the identified group is any number from one through nine. In a still more preferred embodiment, each hydrocarbyl group is a C_1 - C_9 alkyl group, which can be a straight chain, branched chain, or cyclic; or an aromatic group with one or more alkyl substituents. Further, it has been found that surplus (free) neutral ligands (Ls) of formula (a) can be present in the
15 compound from which the deposition vapor is formed without adversely impacting desired results, and may possibly be useful in controlling one or more aspects of nanostructure formation. Organocopper precursors of the type described by formula (a) are further described in U.S. Patent Number 6,538,147 B1 to Choi, which is hereby incorporated by reference.

20 In another more preferred embodiment directed to nanostructure formation with copper, any organometallic composition conforming to formula (a) is utilized for which CVD deposition of copper can be performed at a temperature of 400 °C or less and at a pressure of 1.0 torr or less. In one even more preferred embodiment directed to

nanostructure formation with copper, an organometallic of the following formula (b) is utilized to supply the vapor to chamber 22:



5 where:

L is a trialkyl phosphite.

This compound is particularly suited to CVD of copper with system 20. During this CVD procedure, the vapor decomposes to release copper under appropriate pressure and
10 temperature conditions as previously described in connection with stage 124, and can be evaporated during stage 126 with evaporation device 32 at a temperature of about 100°C. In another embodiment, the vapor may be provided through means other than evaporation with system 20 as would occur to those skilled in the art.

In other embodiments of the present invention, a different process and/or source
15 material other than a compound of the formula (a) or (b) is utilized for nanostructure formation with copper. In further embodiments, nanostructure formation with other noble metals in addition to or as an alternative to copper is desired. As used herein, a "noble metal" refers to one or more of copper, gold, silver, and platinum. Still other embodiments of the present invention are directed to nanostructure formation with other
20 metals and/or materials with or without one or more noble metals.

Conditional 130 of process 120 corresponds to a decision of whether to deposit an oxide of the metal provided from the vapor. If a metal oxide is desired, then oxygen is introduced into chamber 22 in stage 132. If a metal oxide is not desired, then oxygen is

not supplied (stage 132 is skipped), and process 120 proceeds from conditional 130 to stage 140. In embodiments for which oxides are not desired, conditional 130 and stage 132 may not be included in process 120, and correspondingly supply 140 and valve 144 may not be present in system 20. In still other embodiments, process 120 can be adjusted
5 to introduce one or more other types of gaseous material into chamber 22 as an addition or alternative to oxygen.

In stage 140, nanostructures 54 (see FIG. 3) are grown on substrate 52 by depositing material from the organometallic vapor including metal and/or oxygen as appropriate. In alternative embodiments, the introduction of oxygen and/or one or more
10 other any gaseous materials supplied in accordance with stage 132 may be delayed until after the growth of nanostructures 54 has started. For such embodiments, oxygen is only provided during a later portion of nanostructure growth in stage 140. Surprisingly, it has been discovered that a nanostructure 54 comprised of a material including copper can be formed with process 120 from $\text{Cu}(\text{ethylacetoacetate})\text{L}_2$ with $\text{L} = \text{trialkyl phosphite}$,
15 without a catalyst or reducing agent. Moreover, this nanostructure formation is freestanding, with the nanostructures extending away from substrate 52 and being generally aligned along vertical axis V. Referring particularly to FIG. 3, nanostructures 54 made in accordance with process 120 are shown in the form of nanowires 56 each extending from a substrate contact end 60 to a free end 58. Only a few nanowires 56
20 with free end 58 and substrate contact end 60 are designated by reference numerals to enhance clarity of FIG. 3. As stage 140 of process 120 is performed, nanowires 56 are deposited, growing away from substrate surface 62 in a columnar manner along vertical axis V. Nanowires 56 each formed in this matter, have an approximately constant width

or diameter represented by dimension D1. The length of each nanowire 56 is represented by dimension D2. Dimensions D1 and D2 are specifically designated in FIG. 3 only for a leftmost nanowire 56 to preserve clarity.

In one preferred embodiment, dimension D1 is 500 nanometers or less and
5 dimension D2 is at least ten times greater than dimension D1 for each of the nanowires 56 formed. In a more preferred embodiment, dimension D1 is 50 nanometers or less and/or dimension D2 is at least 50 times greater than dimension D1. In an even more preferred embodiment, dimension D1 is 10 nanometers or less. For nanostructures 54 based on the even more preferred deposition vapor formed with process 120 by
10 evaporation of the copper precursor, $\text{Cu}(\text{ethylacetoacetate})\text{L}_2$ with L = trialkyl phosphite, it has been surprisingly found that the resulting nanowires are monocrystalline.

Substrate 52 can be comprised of one or more types of material. In one preferred embodiment, at least the portion of substrate surface 62 in contact with nanostructures 54 is made of a metallic or intermetallic material. In another preferred embodiment, at least
15 the portion of substrate surface 62 in contact with nanostructures 54 is made of a semiconductor material that can be doped or undoped such as silicon, germanium, gallium-arsenide, etc. In yet another preferred embodiment, at least the portion of substrate surface 62 in contact with nanostructures 54 is made of a dielectric material. In one more preferred embodiment, this dielectric form of surface 62 includes silicon
20 dioxide. In still other preferred embodiments, at least a portion of substrate surface 62 in contact with nanostructures 54 is comprised of an organic-based polymer or the like. In yet other embodiments, surface 62 can be comprised of a different material as would occur to those skilled in the art.

Further embodiments include the deposition of nanoparticles on substrate 52 prior to nanostructure growth in stage 140. Under appropriate conditions, such nanoparticles may be used to influence and/or control nanostructure growth. In one preferred form, these deposited nanoparticles are composed of a metal or metal oxide that can be reduced to a metal under reducing ambience. In a more preferred form, such metal and/or metal oxide nanoparticles are of a noncatalytic type with respect to the precursor material utilized for vapor deposition in stage 140. Nanoparticles may be deposited on substrate 52 using solutions containing desired particles or precursor materials by standard processes, such as spraying, dip-coating, spin-coating, or charged liquid cluster beam (CLCB), to name just a few.

In still further embodiments, a metal may be subsequently deposited on nanostructures produced in stage 140. For example, Ag, Ni, Co, and/or Fe may be applied to copper nanowires or other nanostructures by CVD or other standard techniques. In one particular form, copper nanowires are etched prior to CVD application of Ag, Ni, Co, or Fe to reduce/control the copper nanowire diameter.

Nanostructures have numerous industrial applications. Nanostructures 54 produced in stage 140 are utilized in stage 150 of process 120 (see FIG. 2). In stage 150, one or more nanostructures are incorporated into a device. This incorporation is performed using standard techniques and equipment not shown in the FIG. 1 depiction of system 20. Alternatively or additionally, one or more nanostructures are self-assembled into a device of interest as they are formed in stage 140. In one nonlimiting example, substrate 52 is subsequently processed to define other structures/components of a desired device using techniques known to those skilled in the art.

Referring additionally to FIGS. 4-7, a few nonlimiting examples of nanostructure applications are shown. FIG. 4 illustrates integrated circuit (IC) device 220 including one or more nanostructures 54. Such nanoscale elements are useful in providing higher speed electronic components as would be appreciated by those skilled in the art. FIG. 5 illustrates display 230 with a number of field emitters 232 (only one being shown to preserve clarity). In one preferred embodiment, display 230 is of a flat panel type. Emitter 232 includes a number of nanostructures 54 to facilitate smaller and/or higher resolution display capabilities among other things. FIG. 6 illustrates device 240 with one or more nanostructures 54 for processing, receiving, and/or transmitting signals at frequencies of 100 GHz or more. U.S. Patent Nos. 6,440,763 B1 to Hsu; 6,465,132 B1 to Jin; and 6,504,292 B1 to Choi et al. provide additional background information concerning these types of applications. FIG. 7 illustrates sensing device 250 with one or more nanostructures 54. In one form, device 250 is a type of tactile detector that utilizes a set of nanowires as described, for example, in U.S. Patent No. 6,286,226 B1 to Jin. In still other embodiments, nanostructures according to the present invention are utilized as would occur to those skilled in the art.

After incorporation of nanostructures 54 in stage 150, process 120 halts. It should be understood that process 120 can be repeated as desired. Further, process 120 can be integrated into one or more device manufacturing procedures using standard techniques known to those skilled in the art. Alternatively or additionally, system 20 can include one or more programmable or dedicated controllers to regulate desired aspects of process 120 including, for example, operation of subsystems 24 and/or 26, the supply of vapor

from source 30, the provision of oxygen from supply 40, and/or the operation of such other equipment associated with system 20 (not shown) as would be desired.

EXPERIMENTAL EXAMPLES

The following are nonlimiting experimental examples of the present invention and are in no way intended to limit the scope of any aspect of the present invention.

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FIRST EXPERIMENTAL EXAMPLE

An experimental system like that shown as system 20 in FIG. 1 was set-up and utilized to form monocrystalline, copper nanowires on a brass substrate. For this experiment, the copper precursor, $\text{Cu}(\text{ethylacetoacetate})\text{L}_2$ with $\text{L} = \text{trialkyl phosphite}$, was evaporated at approximately 100°C and thermally decomposed to deposit copper on the brass substrate at a temperature of about 300°C . Pressure was between 0.1 and 1.0 torr during deposition. Copper nanowires were formed that extended away from the brass substrate. These copper nanowires were freestanding during formation. FIG. 8 provides a Scanning Electron Microscope (SEM) image of the resulting copper nanowires deposited on the brass surface of the substrate. X-ray Photoelectron Spectroscopy (XPS) demonstrated that the experimentally grown copper nanowires were of a highly pure form, consisting essentially of copper. A graph illustrating the XPS analysis is provided in FIG. 9. Transmission Electron Microscopy (TEM) was preformed to generate an image of the experimentally grown copper nanowires which is provided in FIG. 10. FIG. 10 demonstrated that the copper nanowire structure was of a single crystal (monocrystalline) type. The diameters of the copper nanowires generated in this experiment were each less than 500 nanometers. No catalyst or reducing agent was used to produce the resulting copper nanowires.

Electric field emissions of copper nanowires shown in FIG. 8 were measured. These measurements were as low as 8 volts per micrometer, which is significantly lower than etched metal nanowires of comparable dimensions. Accordingly, suitability of the experimentally grown copper nanowires for higher current emitters of the type desired for flat panel displays and/or high-frequency devices was demonstrated.

SECOND EXPERIMENTAL EXAMPLE

Utilizing the same set-up as the First Experimental Example previously described, and the same type of copper precursor, copper nanowires were deposited on a silicon (Si) substrate instead of brass. The Si substrate temperature was in a range of 200 °C to 400 °C and under a pressure of 0.1 to 1.0 torr during deposition of the resulting copper nanowires. This experiment was performed both with and without an argon carrier gas during chemical vapor deposition. No catalyst or reducing agent was utilized to produce the resulting copper nanowires.

THIRD EXPERIMENTAL EXAMPLE

The same experimental set-up used for the prior described experiments was utilized in a Third Experimental Example except a substrate with a titanium nitride (TiN) surface was utilized and copper nanowires growth thereon. No catalyst or reducing agent was utilized to produce the resulting copper nanowires.

FOURTH EXPERIMENTAL EXAMPLE

The same experimental set-up utilized for the prior described experiments was also utilized to perform the Fourth Experimental Example except that a substrate with a dielectric surface was utilized. This surface was made of silicon dioxide (SiO_2). Copper nanowires were grown on the dielectric substrate. No catalyst or reducing agent was utilized to produce the resulting nanowires. Further, copper nanowires can be grown on other metallic, dielectric, intermetallic, and semiconductor substrates utilizing the teachings of the present invention, including organic-based polymer substrate surfaces, and substrates with surface patterning to define regions composed of different materials.

FIFTH EXPERIMENTAL EXAMPLE

The Fifth Experimental Example was performed with the same set-up as the prior described experimental examples except that oxygen was introduced during processing. The oxygen was not introduced until after initial growth of the copper nanowires had begun. The later introduction of oxygen resulted in the formation of at least a portion of each of the nanowires from copper oxide instead of elemental copper. No catalyst or reducing agent was utilized to produce the resulting copper oxide nanowires.

Any theory, mechanism of operation, proof, or finding stated herein is meant to further enhance understanding of the present invention and is not intended to make the present invention in any way dependent upon such theory, mechanism of operation, proof, or finding. All publications, patents, and patent applications cited herein are
5 hereby incorporated by reference, each in its entirety. While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only the selected embodiments have been shown and described and that all changes, modifications and equivalents that come within the spirit of the invention as defined
10 herein or by the following claims are desired to be protected.